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Photochemistry on, and Nature of Adsorbed Species on

Colloidal Clay and Model Clay Systems

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The concept of the research was to study the photochemistry of molecules adsorbed on aqueous colloidal clay systems and other model systems related to clays. To this end, the nature of the adsorption of molecules of photochemical interest on colloidal montmorillonite and kaolin clays has been studied. Systems that mimic colloidal clays have also been studied, such as colloidal silica. The date obtained and mechanisms of several photochemical reactions in these systems have been established and are listed in the references. The final report summarizes and outlines the significance of early work together with the findings in recent papers.

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Introduction

The concept of the work is to study the photochemistry of molecules adsorbed on aqueous colloidal clay systems and other model systems related to clays. To this end, the nature of the adsorption of molecules of photochemical interest on colloidal montmorillonite and kaolin clays has been studied. Systems that mimic colloidal clays have also been studied, such as colloidal silica. The data obtained and mechanisms of several photochemical reactions in these systems have been established and are listed in the references. This report summarizes and outlines the significance of early work together with the findings in recent papers.

Significance to Army Research Office, ARO.

In their Decon program the ARO is interested in the removal of toxic contaminating chemicals from solid surfaces, and in their subsequent chemical transformation to non-toxic substances. To this end colloidal clay systems and modified clay systems are suggested as suitable "detergent" like or host systems for various materials including toxic substances. Subsequent photochemistry utilising the reactive nature of clays, contributes to the chemical transformation of the materials.

In some instances toxic materials may be embedded in polymer like materials. To this end the research reports experiments on materials that on illumination with light degrade polymers, thereby releasing toxic materials, for solubilisation, and subsequent destruction.

Part I. Photochemical Properties of Clays and Colloid Materials;
Facts Established to Date

References 1 to 6 cover much of our early research work on the photochemistry of materials adsorbed on clays while 7 to 28 cover more recent work. The present discussion outlines the work for convenience, and points out features of the work that are of particular significance.

Colloidal Silica (References 1 & 2)

Photochemical studies on colloidal silica particles were initiated in conjunction with the clay studies, as the former system at least provides a simple model system for clays, and also acts as a bridge between ionic organic micelle systems and colloidal clays. In the first instance a commercial colloidal clay (NALCOAG from the Nalco Co.) was used; and the data are reported in Reference 1. A brief outline of the findings is given below.

Two probe molecules, Ruthenium tris-bipyridyl, $Ru(bpy)_3^{+2}$, and 4-(1-pyrenyl)butyltrimethylammonium bromide, PN^+, were used to investigate the nature of colloidal silica particles in water. The fluorescence spectra of the two probes show that the silica surface is very polar and similar to water. Quenching studies of the excited state of $Ru(bpy)_3^{+2}$ and PN^+ by anionic quenching molecules show that the particles are negatively charged but that the charge is not as effective as that on sodium lauryl sulfate micelles. Quenching studies with cationic quenchers show that cations are bound strongly to the silica particles but do not move as readily around the surface as on anionic micelles. A small steric effect is observed with neutral quenchers which decreases the quenching efficiency. Several charge transfer reactions, including photo-ionization, are strongly affected by the silica particles.

The studies show many similarities to anionic micelles; they differ from micelles in two important aspects: (a) silica particles do not solubilize neutral organic molecules and (b) cationic organic molecules such as PN^+, hexadecyltrimethylammonium bromide, and hexadecylpyridinium chloride, tend to cluster on the silica surface rather than disperse uniformly around it as with ionic micelles.

We have also synthesized our own colloidal silica systems, in order to have quality control over the product, and as a first stage in the synthesis of artificial clay systems. These data are given in Ref. 2 and a brief summary is given below.

A polymerized SiO_2 particle was made which forms colloidal solutions in water; the particle radius is measured as 500 Å by electron microscopy, and also by dynamic light scatter. The probe ruthenium tris(bipyridyl), $Ru(bpy)_3^{+2}$, immediately associates with the surface of the colloid and shows both spectroscopic and kinetic properties that are indicative of the SiO_2-water interface. Incubation for several hours leads to a greatly enhanced phosphorescence yield and lifetime for excited $Ru(bpy)_3^{+2}$, while the spectrum shows a marked blue shift with the appearance of two peaks $\lambda = 5730$ and 6060 Å, in comparison to one at $\lambda = 6130$ Å on the SiO_2 surface. The $Ru(bpy)_3^{+2}$ is bound very tightly to the SiO_2 particle under these conditions. Solutes such as O_2, and nitrobenzene that normally efficiently react with excited $Ru(bpy)_3^{+2}$, are unreactive in this system. However, photoinduced electron transfer occurs between excited $Ru(bpy)_3^{+2}$ and methyl viologen, MV^{2+}, giving rise to MV^+. The kinetics of electron transfer suggest that an electron tunneling mechanism is operative. The $Ru(bpy)_3^{+3}$ that is also formed is readily repaired by electron-transfer agents such as ethylenediaminetetra-acetic acid (EDTA) and triethanolamaine (TEA). The data indicate that

$Ru(bpy)_3^{+2}$ is bound tightly and rigidly just below the SiO_2-interface. The polymerized SiO_2 system leads to the largest yield on electron transfer or photoexcitation of $Ru(bpy)_3^{+2}$ and MV^{2+}, when compared to water, Nalco silica (surface binding of Ru(II) only), and micellar sodium lauryl sulfate (NaLS).

Reference 10 refers to our studies of the photochemistry of the uranyl ion in colloidal silica solutions. This ion was chosen as an alternative to the ruthenium tris(bipyridyl) used in earlier studies, i.e. as a photo-oxidizing agent to oxidize other materials absorbed on the silica systems. The uranyl ion, UO_2^{2+}, is positively charged and adsorbed strongly onto the silica particles. The rates of reaction of excited UO_2^{2+} with several different quenching materials, all of which are due to electron transfer, are only slightly affected by the absorption of UO_2^{2+} to the silica system. However, the lifetime of the excited state is greatly increased, up to 440 microseconds on the silica particles compared to 11 microsecond in water, thus ensuring efficient reaction with other molecules. Other materials such as micelles unfortunately shorten the UO_2^{2+} lifetime as they react with the excited UO_2^{2+}. Hence, the silica system provides a good host medium for the UO_2^{2+} as it increases its life time and provides a template which enhances reactions with other species.

Reference 16 refers to our work in a silica gel matrix. The concept of this work is to provide a medium for the excited state chemistry that can be applied over a solid surface, and be maintained there while photochemical reactions occurs. Fluid solutions of surfactants or water tend to run off the surface and the photochemical reactivities are reduced. It has been shown that silica is a very good host medium for many photo-systems. Silica gel systems are constructed with one of three photo-systems i.e ruthenium tris bipyridine, uranyl ion, or pyrenetrimethylammomium bromide. The reactivities

of the above excited states with various anions, cations and neutral quenchers were studied. In the silica gels the above cationic molecules exhibit properties similar to those in porous silica, and unlike those involved in bulk water. The subsequent reactions of all bound probes and quencher are explained in terms of electrostatic interactions of the gel network and the reactants. The SiO_2 gel system provides a method of maintaining a reactive photochemical system in contact with a surface such as a polymer for extended periods of time, so that photochemical damage to the polymer can be maximised.

Important Features of the Silica Work

The data from the silica studies are high lighted by comparison with the more familiar anionic micellar systems such as sodium lauryl sulfate. The following features stand out and are important for the subsequent clay studies.

(a) The inorganic nature of the colloidal silica does not provide suitable host sites for non-charged organic molecules.

(b) Cationic molecules, whether inorganic or otherwise, are strongly adsorbed to the silica surface.

(c) Photo-induced reactions of the species from (b) are explicible in terms of knowledge established with anionic micelles.

(d) Cationic organic molecules tend to segregate on the silica surfaces and not distribute themselves uniformly amongst the particles in a Poisson type of distribution. This is quite unlike what is known for anionic micelles.

(e) The nature of the adsorption site in silica particles depends on the preparation of the system; a point to be watched for when dealing with clays.

(f) The use of the gel form of SiO_2 enables photomaterial to be kept in close contact with a solid surface.

This is in marked contrast to fluid systems e.g. micelles which tend to run off the surface.

Clay Systems

Studies in colloidal clay systems have been published in references 3, 4, and 6, which are connected with earlier work and in ref. 11, 14, 19, 20 and 25 connected with recent work. A brief description of the finding is given below.

For many years clay minerals have been the focus of intensive research due to their ability to intercalate various molecules and their catalytic properties. The two minerals studied in earlier work were montmorillonite and kaolin. Montmorillonite possesses a layered structure and strong adsorptive properties due to the expandability of its internal layers. It is commonly referred to as a 2:1 layer mineral indicating that an aluminum in octahedral configuration shares oxygen atoms with 2 silica sheets in tetrahedral configuration, one on each side. Kaolin, on the other hand, is a nonexpandable 1:1 layer mineral, i.e., there is a sharing of oxygen atoms between one silica sheet and one aluminum sheet in a continuous network that cannot be easily disrupted for the intercalculation of ions or organic molecules. Hence, only the surface of kaolin particles participates in chemical reactions whereas both the surface and the internal layers are available in montmorillonite particles.

Montmorillonite has been shown to induce the thermal transformation of alkylammonium ions adsorbed on its surface at temperatures well below the thermal decomposition temperature of the amine. The mechanism is attributed

to that of acid catalysis due to the highly acidic nature of the montmoril-lonite surface ($k_W \cong 10^{-8}$). The extreme acidity of the "dry" mineral surface is postulated to be due to the polarization of residual water molecules by the exchangeable cations also located at the mineral's surface.

Both montmorillonite and kaolin have been shown to catalyze the poly-merization of some unsaturated organic compounds such as styrene and hydroxyethyl methacrylate and yet to inhibit polymer formation from other structurally related monomers such as methyl methacrylate. This behavior is believed to be due to the electron accepting or electron donating sites on the clay mineral. The electron acceptor sites are thought to be aluminum at the crystal edges and transition metals, such as iron, in an oxidized valence state in the silicate layer. Correspondingly, the electron donor sites are transition metals in the reduced state. The aluminum sites at the crystal edges arise from defects or fissures in the crystal structure of the clay. It has been suggested that the catalytic activity at this site is due to aluminum in octahedral coordination with the mineral acting as a lewis acid.

The presence of transition metals is due to isomorphous substitution within the lattice structure of the clay mineral. This involves the replace-ment of quadrivalent silicon in the tetrahedral sheet with trivalent species such as aluminum or ferric ion. In the octahedral sheet, aluminum may be replaced by divalent iron or magnesium. The small size of these atoms permits them to take the place of the Si and Al atoms. The replacement of an atom of higher positive valence for one of lower valence results in a net negative charge. This excess of negative charge is balanced by the adsorption of cations on the layer surfaces. In the presence of water, these charge-balancing cations may be exchanged with other cations available in solution. Of course, the cation exchange capacity is greater for montmorillonite due to

the possibility of exchange in the internal layers.

The property of cation replaceability in clays has been extensively studied and is responsible for many of the unique properties of montmorillonite and kaolin. Past work (3,4,5, and 6) made use of the cation exchange capacity (cec) by exchanging tris(2,2'-bipyridinium) ruthenium(II), $Ru(bpy)_3^{+2}$, for the clay Na^+ ions. This process locates a luminescent probe molecule on the clay and enables us to gain information about: (1) the mobility of the probe on the clay particle, (2) the accessibility of various quenchers to the probe and (3) the local environment of the probe and the nature of the colloidal clay particle.

Photochemical reactions have been studied in aqueous colloidal montmorillonite and kaolin clays. The photochemical probe used is Ruthenium tris(2,2'-bipyridyl) $Ru(bpy)_3^{+2}$, which is quenched by the molecules Cu^{+2}, Eu^{+3}, nitrobenzene and dimethylaniline. The processes are dynamic with k_q equal to 1.9 x 10^7 $M^{-1}s^{-1}$, 1.2 x 10^8 $M^{-1}s^{-1}$, 1.9 x 10^8 $M^{-1}s^{-1}$ for Cu^{+2}, nitrobenzene and dimethylaniline, respectively. The absorption and emission spectroscopy at room temperature and 77° K of $Ru(bpy)_3^{2+}$ comments on the environment of the probe on the kaolin surface and in the montmorillonite layers. Quenching occurs when the quenchers are adsorbed into the layers (Langmuir type) or react from the bulk solution with the probe located on the surface. The rate data show that both the cationic and uncharged molecules move quite freely on the clay surfaces and also in the clay layers. Inert electrolytes such as KCl markedly affect the kinetic data in montmorillonite colloids by decreasing the particle association.

Organo-Clays

Organo-clays have been constructed using cetyltrimethyl ammonium bromide,

CTAB, and dodecyl alcohol as additives to the clay. Layers of organic material are formed by these additives in montmorillonite layers, and now non-ionic organic molecules such as pyrene are readily adsorbed by these organo-clays. The quenching of excited pyrene and several of its derivatives on organo-clays have been studied with molecules that reside within the clay layers that are adsorbed on the clays, and that reside mainly in the aqueous phase. The data have been used to interpret the nature of the adsorption process and the relative ease of movement of molecules in these systems.

Organic cations such as Rhodamine B, PN^+, etc., are strongly adsorbed onto the colloidal clays, but excitation of these molecules with UV or visible light does not lead to fluorescence as the excited states are quenched and subsequently decomposed by the clay. The probe molecule pyrene-butyl-trimethyl ammonium bromide (PN^+), upon excitation fluoresces well on anionic micelles, silica particles and in water, but is severely quenched when adsorbed on the clay particles. Fluorescence does appear, however, upon addition of cationic surfactants such as cetyltrimethyl ammonium bromide (CTAB). Short chain quaternary ammonium compounds, e.g., tetramethyl or tetraethylammonium bromide are not effective in increasing PN^+ fluorescence on the clay. It is concluded that CTAB is adsorbed in the vicinity of PN^+ and insulates the excited $(PN^+)*$ from the clay thereby preventing its photode-composition and promoting fluorescence.

Addition of a quenching cation, e.g. cetylpyridinium chloride (CP^+), decreases the fluorescence of the PN^+/clay/CTAB system via static quenching. The data clearly show the segregation of the adsorbed organic material on the clay surface, a feature noted previously in SiO_2 particles.

Photochemical Oxidation with Clays

It is stated in the literature that aromatic amines (such as Benzidine BD, and tetramethylbenzidine TMB), are thermally oxidised on clays suspended in non-polar solvents such as hexane. If water or water-alcohol mixtures are used as solvents, then thermal reaction does not occur, but photochemical association occurs quite readily to yield products that are identical to those observed in the thermal studies.[11] A brief summary is given below.

Photolysis ($\lambda < 4000$ Å) of BD or TMB in aqueous or alcohol-water mixtures in the presence of colloidal clay leads to a green colored solution. Flash studies indicate that the initial photochemical event is photo-ionization in the bulk aqueous phase,

$$TMB \xrightarrow{\;h\nu\;} TMB^+ + e^-_{aq}$$

as both TMB^+ and e^+_{aq} are observed spectroscopically. The hydrated electron reacts rapidly ($\tau \frac{1}{2} < \mu$ sec) with O_2 giving O_2^-; TMB^+ has a much longer lifetime ($\tau > 1$ m sec) which is shortened in the presence of clay, when the spectrum characteristics of TMB^+ ($\lambda_{max} = 4700$ Å) is replaced with a spectrum with λ_{max} at 3900 Å and 6250 Å. The resulting species is bound tightly to the clay and is most probably cationic in nature. It also exhibits an EPA signal, which unfortunately is too broad for identification purposes. Addition of acid to the sample changes the color of the clay from green to orange, the color of the dication, TMB^{++}, and the EPR signal disappears. This is typical of the behavior of TMB^+ in micellar NaLS solutions. The studies show that TMB^+ is captured by the anionic clay, whence the TMB^+ - clay interaction gives rise to a dimer of TMB^+.

Photocatalytic decomposition of the simulant mechlorethamine (MEA) and other dye molecules has been observed in aqueous and colloidal solution. The decomposition of MEA upon UV irradiation (λ peak = 300 nm) was monitored by

measuring the amount of Cl^- produced. MEA decomposes gradually in water on UV irradiation; 10% of MEA was decomposed after 1 hr. irradiation, 40% after 3 hrs. However, the addition of laponite which has a CTAB double layer on its surface markedly improved the decomposition efficiency; 35% after 1 hr and 90% after 3 hours irradiation. The addition of benzidine, which acts as an electron donor on excitation, also dramatically increased the decomposition rate to 45% after 10 min.

Surface Configuration

Recent clay[21,22] studies have been aimed towards identifying the nature of the configuration of adsorbed molecules on clay surfaces, and how the surface geometry controls the photochemistry. Steady-state and time-resolved fluorescence quenching studies of the fluorescence quenching of 4-(1-pyrenyl)butyl-trimethylammonium ion, (PN^+), adsorbed on colloidal laponite clay by co-adsorbed alkylpyridinium ions showed unusual behaviors. Increasing the quencher concentration at first led to an efficient quenching of PN^+ fluorescence, but on increasing the quencher concentration further a reverse effect is observed, whereby the fluorescence started to recover, only to be followed by a smaller degree of quenching. The degree of recovery was strongly dependent on the chain length of the alkyl pyridinium ions; the longer the chain length the larger the degree of recovery. PN^+ fluorescence was also quenched by laponite clay itself or cupric ion in copper-clay, where cupric ion was constructed in the clay lattice. However, co-adsorbed hexadecyltrimethylammonium (CTAB) cations dramatically reduced the quenching. These results can be explained in terms of the change of geometrical arrangement of PN^+ adsorbed on clay.

Quenching of PN^+ fluorescence by dimethylaniline, nitrobenzene, and

nitromethane in CTAB-laponite system obeyed Poisson type kinetics, indicating that the adsorbents exist in the form of clusters or zones on the clay surface.

The fluorescent probe Ruthenium tris(2,2'-bipyridyl), $Ru(bpy)_3^{2+}$ has also been used to investigate the nature of the surfaces of the following clays; laponite, which is a synthetic clay, and natural hectorite and montmorillonite. $Ru(bpy)_3^{2+}$ is adsorbed completely via the clay by ion exchange and on excitation gives rise to a luminescence spectrum in the red part of the spectrum with a lifetime of about half a microsecond. The lifetime, quantum yield, and nature of the absorption spectrum are dependent on whether the $Ru(bpy)_3^{2+}$ is adsorbed in layers as in the natural clays or whether it is adsorbed on the surface as with laponite. At low concentrations of laponite, $Ru(bpy)_3^{2+}$ is adsorbed on outer layers and is in contact with the aqueous phase. However, at higher clay concentrations or in the presence of calcium chloride, layering of the clay occurs and the probe molecule is placed progressively between the layers where its photophysics is altered. The casting of a film from the laponite-$Ru(bpy)_3^{2+}$ exhibits maximum spectral change as associated with maximum colloid layer formation. Such changes are not as readily observed with hectorite or montmorillonite, and this indicates that, for the most part, these systems exist as layered colloids and that $Ru(bpy)_3^{\pm 2}$ is already adsorbed between the layers. Other molecules such as Cu^{2+}, dimethylaniline, and nitrobenzene react with excited $Ru(bpy)_3^{\pm 2}$ through electron-transfer reactions and are also adsorbed to varying extents on the clay surface. Cu^{2+} is adsorbed strongly and the kinetics are simplified due to the strong adsorption. Here, Stern-Volmer type kinetics are observed and a quenching rate constant is obtained which is lower than that in the aqueous solution, which gives an estimate of the degree of movement of cupric ions on

the clay surface. Dimethylaniline and nitrobenzene are adsorbed weakly on the clay. However, the clay catalyzes the reaction of the $Ru(bpy)_3^{+2}$ with these quenchers as both are adsorbed in a small volume, i.e., the clay surface. The kinetics that describe these latter reactions are of the Poisson form, and the kinetics indicate that the reactive quencher molecules are adsorbed around the $Ru(bpy)_3^{2+}$, in a zone like effect, rather than being adsorbed randomly throughout the system. This tends to indicate that the sites of adsorption are not uniform on the clay surface but occur in regions.

Laponite clay colloids have also been constructed with double layers of cationic surfactants. This reverses the natural negative charge of the clay surface and produces an organic layer of approximately 35 A on the clay surface. Hydrophobic molecules are readily adsorbed into this layer and are in close contact with the active clay surface. The surfactant layer vastly improves the power of the clay colloid to adsorb hydrophobic material.

Important Features of the Clay Work

The data from the clay studies are highlighted by comparison with the earlier colloidal silica systems and anionic micelles.

   (a) As in the silica system non-polar organic molecules are not strongly adsorbed in the clays. However, organo-clays provide a suitable medium for solubilisation of these materials.

   (b) Unlike the silica systems polar organic molecules e.g. nitrobenzene etc. are strongly adsorbed by colloidal clays.

   (c) As in the silica systems cationic species are adsorbed to colloidal clays; in some cases e.g. Ruthenium tris-bipyridyl, the adsorption is so strong that the cations cannot be removed. Such adsorption is much stronger than that in SiO_2 systems.

(d) As in silica systems organic cations adsorbed on clays tend to cluster together forming colonies of organic material. The material may be dispersed by addition of cationic surfactants.

(e) Unlike silica systems, clays are very reactive towards adsorbed species. The photo-activity is associated with lattice bound ferric or cupric ions, which may oxidise adsorbed species. Thus, clays participate strongly in the photooxidation of adsorbed molecules.

(f) Photo induced reactivity between adsorbed molecules is strongly promoted in layered clays such as montmorillonite, and synthetic clays such as laponite.

(g) Colloidal clays also participate in photo oxidation reactions that occur in the bulk aqueous phase, by removing photo-produced cations, via very strong solute-clay interaction. In most cases it is not possible to desorb these cations from the clays.

(h) The organisation of the adsorbed molecules on clay surfaces controls the efficiency of their reactions. This is unlike silica or micellar colloids.

Polymer Interactions

It is stated that many chemical contaminents of interest to ARO are embedded in a polymer matrix on the surface to be decontaminated. The polymer matrix makes it difficult to extract the contaminant and hence to solubilize it in the designed environment, either surfactant or colloidal clay systems. We have initiated studies of photochemistry in polymeric systems in order to address this problem. The aim of this project is to understand the photochemistry of systems of interest e.g. $Ru(bpy)_3^{2+}$ and methyl viologen, in polymer films, and to investigate photosystems which degrade polymers.

The initial studies in cellulose films are given in references 17 and 18.
A brief summary of the work is given below.

Ruthenium tris (2,2'-bipyridyl), $Ru(bpy)_3^{2+}$, was adsorbed into a cellulose
film and the excited triplet state decay was studied at 77 K and 295 K using
Laser photolysis techniques. The triplet (denoted as *Ru(II) decay depends on
both $Ru(bpy)_3^{2+}$ concentration and laser pulse intensity, and follows the
equation,

$$- \frac{d[*Ru(II)]}{dt} = k_1[*Ru(II)] + k_2[*Ru(II)][Ru(II)] + k_3[*Ru(II)]^2$$

At room temperature the rate constant k_1, which corresponds to the inherent
unimolecular decay, is $(8.8 \pm .5) \times 10^5 s^{-1}$, $k_2 = (7.8 \pm .8) \times 10^6 mol^{-1}dm^3s^{-1}$,
and corresponds to quenching by $Ru(bpy)_3^{2+}$ ground state, and $k_3 = (5.2 \pm .6) \times$
$10^7 mol^{-1}dm^3s^{-1}$ and corresponds to triplet-triplet annihilation which is
followed by electron transfer. Charge separation arising from the quenching
process is found to be small. In order to facilitate the interpretation of
the above processes, similar experiments were accomplished in water and water-
glycerol mixtures. The rate constants, obtained in aqueous solutions for
$Ru(bpy)_3^{+2}$ ground state quenching and triplet-triplet annihilation, are $(5.1 \pm$
$.6) \times 10^7 mol^{-1}dm^3s^{-1}$ and $(1.1 \pm .3) \times 10^8 mol^{-1}dm^3s^{-1}$ respectively; details of
the reaction mechanism are also given.

Photoinduced reactions of methyl viologen, MV^{2+}, have been studied in
cellophane by steady state and pulsed laser techniques. The reduced form MV^+
is produced on irradiation, due to e^- abstraction from cellophane. The
reduced form is quite stable for hours in aerated cellophane, unlike similar
studies in liquid water or alcohols. Small amounts of H_2O reduce the
reactivity of MV^{2+} and cellophane, and promote the formation of the MV^+/MV^{2+}

complex.

We have also made attempts to synthesise semiconductors in polymer films. In particular cadmium sulfide has been synthesized in nafion. This perhaps illustrates quite clearly that the photochemistry of many systems is quite different in polymer film as compared to simple solution. In the case of the cadmium sulfide in nafion we found quite different photophysical properties for the cadmium sulfide.[8] In order to fully develop the concepts of these systems we also had to carefully control the preparation of the cadmium sulfide, in some examples given in reference 7 we show that different preparations for cadmium sulfide give rise to quite different materials; later references also refer to this. This work shows that it is indeed possible to promote certain photochemical reactions in rigid media such as polymer films, and that the resulting photochemistry differs from that observated in solution. The next phase in these studies is to investigate the mode of interaction of photosystems with the polymer matrix itself. Some studies along these lines have already been done with methyl viologen.

Polymers such as polymethacrylic acid, PMA, have also been used to coat and stabilise colloidal particles[24]. The polymers which are polyanions produce a net negative on the colloid surface, and enable cationic species e.g. Ruthenium tris bipyridyl to adsorb to the surface. This leads to photo-induced electron transfer between the adsorbed cation and the colloid, a situation which does not take place in the absence of the polymer. Several colloids, TiO_2, ZnO, WO_3, etc. on photo excitation lead to breakdown of PMA adsorbed to the colloid surface, and provides another method of photodegrading polymers. The configuration of the polymer adsorbed on a colloid surface has been studied by the use of polymers containing covalently linked fluorescent chromophores[15]. These polymers are synthesised by copolymerisation of the

monomer and pyrene acrylic acid to give one pyrene molecule per 3000 monomer units. The spectroscopy of the pyrene probe comments back to the behavior of the polymer on the colloid surface. This work is now being extended to several polymers and colloidal systems.

Summary

The initial polymer work shows that in many systems, aqueous colloids or semiconductor colloids can lead to rapid degradation of polymers in solution. On the other hand materials embedded into a polymer matrix, such as ruthenium tris bipyridine, methylviologen, and cadmium sulfide in solid cellophane films, can also promote photochemical reactions which leads to degradation of cellulose. The kinetics of the photochemical reactions are modified compared to homogeneous solutions.

Systems of Additional Interest

Several different systems were studied which are connected with either the silica or clay systems. Our aim was to improve photochemical reactions by using these systems in particular photoinduced reductions. One system is cadmium sulfide deposited in a polymer film, or stabilised by colloidal silica or colloidal clay. Methyl viologen is often used as an electron acceptor in our photosystems in conjunction with CdS or Ruthenium tris bipyridyl. The net products of cation and reduced methyl viologen MV^+ cause further redox chemistry. A major problem with all systems is the back reaction of the ionic products. To prevent this ethylene diamine tetraacetate, EDTA is used to "repair" the cation and release the reduced methyl viologen. We have studied this system further in reference 9, where EDTA is found to form a complex with MV^{2+} with a resultant negative charge. This complex readily attaches to

positively charged surfaces or colloids. Photoinduced electron transfer from CdS stabilised by cationic surfactants to MV^{2+} - EDTA complex given rise to reduced methyl viologen Mv^+., the complex with EDTA dissociates and the positively charged Mv^+. is repelled from the cationic surface. The quantium yields for reactive photo-products is markedly increased.

A further problem that is frequently encountered is that the host materials (colloidal clays and silica) for the photosystems, do not efficiently adsorb non-charged species. This may be rectified by using chromatographic silica, or porous vycor. Reference 19 reports that cadmium sulfide can be formed in porous vycor which also absorbs the cationic species and nonionic organic materials of interest. These studies showed that the photophysical properties of CdS were markedly modified in the constrained host, Vycor glass, where the 30A pores or channels forced the formation of small CdS particles. Two dimensions corresponding to the cross section of the glass pore were less than 30 A while the dimension along the channel was considerably greater. Some semiconductor properties normally associated with large crystals were absent in the CdS-Vycor material. The concept of dimensions was developed further in reference 26 where reversed micelles were used to make cadmium sulfide of very small dimensions. Reversed micelles contain small water pools of 15 A radius where the CdS is precipitated. The smallest particles made in these systems consist of about 4 molecules of cadmium sulfide. These CdS particles exhibit spectroscopic properties which are quite unlike those associated with large single crystal semiconductors. These CdS particles exhibit molecular properties while the lifetimes of CdS excited states are much longer than those associated with bulk CdS. The materials are also more photo-reactive. This area of recent research has been pursued in clay systems further in references 27, 28.

Finally, reference 25 reports on the use of chromatography silica to adsorb noncharged materials such as pyrene for subsequent photochemical studies. The nature of the adsorption process is quite unlike that with colloidal silica and colloidal clay which adsorb non-cationic materials only weakly. In the clay systems adsorption of the organic materials was enhanced by using surfactant systems to create an organic phase on the silica. Chromatography silica possesses a significant number of OH surface groups where pyrene and other hydrophobic materials are efficiently adsorbed. It is important to determine the nature of the organization of the silanol OH groups on the SiO_2 surface, and how they affect the adsorption process. To this end we have developed a probe aminopyrene, AP, which exhibits two distinct spectroscopic regimes, one involved with the free amino form, and one involved with the protonated form. It has been established that with many silicas where the surface OH groups are in close proximity or geminal in nature that AP is adsorbed in the protonated form, whereas isolated OH groups cause adsorption of AP in the free amino form. Acid catalysis via protonation is one of the main catalytic features of clays. The probe AP enables us to assess surfaces for geminal OH groups which lead to acid catalysis.

References

1. Wheeler, J. and Thomas, J. K., ACS Symposium Series 177, Inorganic Reactions in Organized Media, Ed., Smith L. Hold, Amer. Chem. Soc. 97-111 (1982).

2. Wheeler, J & Thomas, J. K., J. Phys., Chem. 86, 4540 (1982).

3. DellaGuardia, R.; Thomas, J. K., Proceeding of Aberdeen Conference on Decontamination (1982).

4. DellaGuardia, R.; Thomas, J. K., J. Phys. Chem. 87, 990 (1983).

5. DellaGuardia, R.; Thomas, J. K., J. Phys. Chem. 87, 3550 (1983).

6. DellaGuardia, R.; Thomas, J. K., J. Phys. Chem. 88, 964 (1984).

7. Kuczynski, J.; Milosavljevic, B.; Thomas, J. K., J. Phys. Chem. 87, 3368 (1983).

8. Kuczynski, J. P.; Milosavljevic, B. H.; Thomas, J. K., J. Phys. Chem. 88, 980 (1984).

9. Kuczynski, J. P.; Milosavljevic, B. H.; Lappin, A. G.; Thomas, J. K., Chem. Phys. Letts. 104, 149 (1984).

10. Wheeler, J.; Thomas, J. K., J. Phys. Chem. 88, 750 (1984).

11. Kovar, L.; DellaGuardia, R.; Thomas J. K., J. Phys. Chem. 88, 964 (1984).

12. Wheeler, J.; Thomas, J. K., J. Photochem. 28, 285 (1985).

13. Kuczynski, J.; Thomas, J. K., Langmuir, I, 158 (1985).

14. Atik, S.; Kuczynski, J.; Milosavljevic, B. H.; Chandrasekaran, K.; Thomas, J. K., Macro- and Microemulsions 20, 303 (1985).

15. Harrop, R.; Williams, P. A.; Thomas J. K., J. Chem. Soc., Chem. Commun. 1366, 280 (1985).

16. Thomas, J. K.; Wheeler, J., J. of Photochem. 28, 285 (1985).

17. Milosavljevic, B.; Thomas, J. K., J. Phys. Chem. 87, 616 (1983).

18. Milosavljevic, B.; Thomas, J. K., Int. J. Radiation Chemistry & Physics 23, 237 (1984).

19. Kuczynski, J.; Thomas, J. K., J. Phys. Chem. 89, 2720 (1985).

20. Chandrasekaran, K.; Thomas, J. K., J. Colloid and Interface Sci. Vol. 106, No. 2, 532, (1985).

21. Nakamura, T.; Thomas, J. K., Langmuir, I, 568 (1985).

22. Nakamura, T.; Thomas, J. K., J. Phys. Chem. 3, 234 (1987).

23. Stramel, R.; Thomas, J. K., J. Coll. & Interface Sci. 110, 121 (1986).

24. Stramel, R.; Thomas, J. K., J. Chem. Soc. Faraday I. 82, 799 (1986).

25. Hite, P.; Krasnansky, R.; Thomas, J. K., J. Chem. Phys. 90, 5795 (1986).

26. Lianos, P.; Thomas, J. K., Chem. Phys. Letts. 125, 299 (1986).

27. Thomas, J. K. J. Phys. Chem. 91, 267 (1987).

28. Stramel, R. D.; Nakamura, T.; and Thomas, J. K. Chem. Phys. Letts. 130, 423 (1986).

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